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The Clar covering polynomial of hexagonal systems III ☆

Heping Zhang[a,*], Fuji Zhang[b]

[a] *Department of Mathematics, Lanzhou University, Lanzhou, Gansu 730000, People's Republic of China*
[b] *Department of Mathematics, Xiamen University, Xiamen, Fujian 361005, People's Republic of China*

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Abstract

The Clar covering polynomial is a recently proposed concept of hexagonal systems by which some important topological indices such as perfect matching count, Clar number, first Herndon number, etc., can be easily obtained. In this paper we establish a relationship between the Clar covering polynomial and sextet polynomial. A lower bound of the Clar number and some properties of coefficients of the Clar covering polynomial are thus deduced. It is mentioned that the summation of coefficients of Clar covering polynomial can be used to calculate the number of perfect matchings of a certain kind of polyominoes relating to crystal physics.

A hexagonal system is a finite connected plane graph without cut vertices in which every interior face is bounded by a regular hexagon of side length 1. Since a hexagonal system with at least one perfect matching may be regarded as the skeleton of a benzenoid hydrocarbon molecule, various algebraic and combinatorial properties of hexagonal systems have been extensively treated by mathematicians and chemists. In what follows, we restrict our consideration to hexagonal systems with perfect matchings.

Let us recall some concepts. Let H be a hexagonal system with perfect matchings. A Clar cover of H is a spanning subgraph of H each (connected) component of which is either a hexagon or an edge. In particular, a Clar cover of H containing no hexagons is a perfect matching of H. A resonant pattern of H is a set of hexagons of a Clar cover of H. A resonant pattern of H is said to be a Clar formula of H if it has the maximum number of hexagons, which is called the Clar number and denoted by $C(H)$

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* Corresponding author. Tel.: +86-931-8912483; fax: +86-931-8911100.
E-mail address: zhanghp@lzu.edu.cn (H. Zhang)

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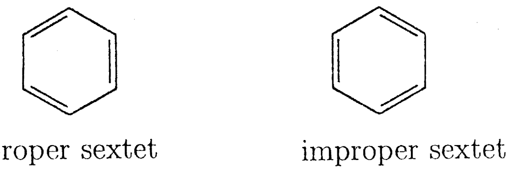

Fig 1

[4,10,13]. The sextet polynomial of H is defined as [6]

$$B(H,x) = \sum_{i=0}^{C(H)} s(H,i)x^i,$$

where $s(H,i)$ denotes the number of resonant patterns having precisely i hexagons and x is an indeterminate or weight associted with hexagons of H. The Clar covering polynomial of H is defined as [15,12,14]

$$P(H,w) = \sum_{i=0}^{C(H)} \sigma(H,i)w^i,$$

where $\sigma(H,i)$ denotes the number of Clar covers of H having precisely i hexagons and w is an indeterminate or weight associted with hexagons of H. It is known that $\sigma(H,0) = K(H)$ is the number of perfect matchings of H, $\sigma(H,1) = h_1(H)$ is the first Herndon number and $\sigma(H,C(H)) = s(H,C(H))$. The Clar covering polynomial of hexagonal systems can be used to produce a general recurrence method for calculating the Clar number. To date, an efficient algorithm for finding a Clar formula of hexagonal systems is still an open problem. In this paper we study further properties of Clar covering polynomial of hexagonal systems.

In order to simplify the disscusion, a hexagonal system H in question is to be drawn in the plane so that a pair of edges of each hexagon lie in parallel with the vertical line. Let M be a perfect matching of H. A cycle C of H is called an M-alternating cycle if the edges of C appear alternately in M and $E(H)\backslash M$, where $E(H)$ denotes the edge-set of H. An M-alternating hexagon of H is called a proper sextet if the extreme right vertical edge belongs to M; an improper sextet otherwise, which are illustrated in Fig. 1.

Denote by $a(H,i)$ the number of perfect matchings of H which contains precisely i proper sextets for $0 \leqslant i \leqslant C(H)$.

Lemma 1. *Let H be a hexagonal system with a perfect matching. Then $a(H,i)$ has the following properties*:

(i) $\sum_{i=0}^{C(H)} a(H,i) = K(H)$.
(ii) $a(H,i) > 0, 0 \leqslant i \leqslant C(H)$, *and*
(iii) $a(H,0) = 1$.

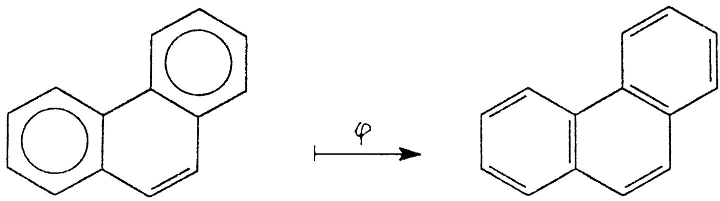

Fig 2

Proof. (i) follows immediately by the definition. For any given i $(0\leqslant i\leqslant C(H))$, assume that S is a resonant pattern of H having precisely i hexagons. Put $H_S := H - V(S)$. It is clear that either H_S has a perfect matching or H_S is empty (without vertices). It is known that (cf. [11]) perfect matchings of H_S form a rooted directed tree structure and the root corresponds to a unique perfect matching M_0 of H_S such that H_S has no proper M_0-alternating cycle (i.e. the extreme right vertical edge of the cycle belongs to M_0), which implies that H_S has no proper sextet with respect to M_0. Let M_1 be a perfect matching of S such that each hexagon of S is a proper sextet. Thus M_0 and M_1 compose of a perfect matching of H and S is the set of proper sextets of H with respect to $M_0\cup M_1$. Hence $a(H,i)>0$ for all $0\leqslant i\leqslant C(H)$. In particular, if $i=0$, $H_S=H$ has a unique perfect matching without proper sextets [1], i.e. $a(H,0)=1$. □

Theorem 2. *Let H be a hexagonal system with a perfect matching. Then the Clar covering polynomial $P(H,w)$ of H can be expressed in the following form*:

$$P(H,w)=\sum_{i=0}^{C(H)}\sigma(H,i)w^i=\sum_{i=0}^{C(H)}a(H,i)(w+1)^i.$$

Proof. Let C be any Clar cover of H. The hexagons of C are transformed simultaneously into proper sextets and the single edge components of C remain unchanged to produce a perfect matching M of H. This defines a mapping from the Clar covers onto perfect matchings as $\varphi : C \mapsto M$, as illustrated in Fig. 2. Let $\mathscr{C}$ denote the set of Clar covers of H. Put $\mathscr{C}_M := \{C\in\mathscr{C}\colon \varphi(C)=M\}$, which give naturally a partition: $\mathscr{C}=\bigcup_M \mathscr{C}_M$, where M goes over all perfect matchings of H. Let M be any given perfect matching of H and i be the number of proper sextets of M, $0\leqslant i\leqslant C(H)$. Each proper sextet of M corresponds to a hexagon or to the three edge components of Clar covers in $\mathscr{C}_M$. Since the weights of a hexagon and an edge of a Clar cover are w and 1, respectively. By rules of sum and product on combinatorics we have that $\sum_{C\in\mathscr{C}_M} w^{h(C)}=(1+w)^i$, where $h(C)$ denotes the number of hexagons of C. Since $a(H,i)$ is the number of perfect matchings having precisely i proper sextets. Then

$$P(H,w)=\sum_{C\in\mathscr{C}} w^{h(C)}=\sum_M\sum_{C\in\mathscr{C}_M} w^{h(C)}=\sum_{i=0}^{C(H)} a(H,i)(w+1)^i. \qquad \square$$

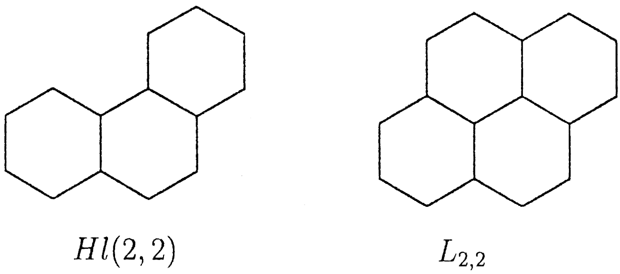

Fig 3

By virtue of the above transformation, we begin to discuss some relations among the coefficients of the Clar covering polynomial. As an immediate consequence of Theorem 2, we have:

Corollary 3. (i) $\sigma(H,i) = \sum_{k=i}^{C(H)} a(H,k)\binom{k}{i}$, $i = 0,\dots,C(H)$; *in particular*, $a(H,C(H)) = \sigma(H,C(H))$,

(ii) $a(H,j) = \sum_{k=j}^{C(H)} \sigma(H,k)\binom{k}{j}(-1)^{k-j}$, $\quad j = 0,\dots,C(H)$.

Theorem 4. *Let H be a hexagonal system with a perfect matching and $C = C(H)$. Then*

$$\sigma(H,C) < \sigma(H,C-1) < \cdots < \sigma\left(H, \left\lceil \frac{C-1}{2} \right\rceil\right).$$

Proof. For $i \geqslant (C-1)/2$ and $i+1 \leqslant k \leqslant C$ it follows that $\binom{k}{i} - \binom{k}{i+1} \geqslant 0$ from the property of the binomial numbers. By Corollary 3(i) we thus have:

$$\begin{aligned}
&\sigma(H,i) - \sigma(H,i+1)\\
&\quad = \sum_{k=i}^{C(H)} a(H,k)\binom{k}{i} - \sum_{k=i+1}^{C(H)} a(H,k)\binom{k}{i+1}\\
&\quad = a(H,i) + \sum_{k=i+1}^{C(H)} a(H,k)\left[\binom{k}{i} - \binom{k}{i+1}\right]\\
&\quad \geqslant a(H,i) > 0. \qquad \square
\end{aligned}$$

Theorem 5. *Let H be a hexagonal system with a perfect matching and $C(H) \geqslant 2$. Then $\sigma(H,1) \geqslant \sigma(H,0)$ and the equality holds if and only if H is either a hexagonal chain $Hl(2,2)$ or a parallelogram $L_{2,2}$ (see Fig. 3).*

To prove the theorem, let us first introduce some important concepts and basic facts. Let H be a hexagonal system with a perfect matching. An edge of H is said to be a fixed single (double) edge if it belongs to none (all) of the perfect matchings

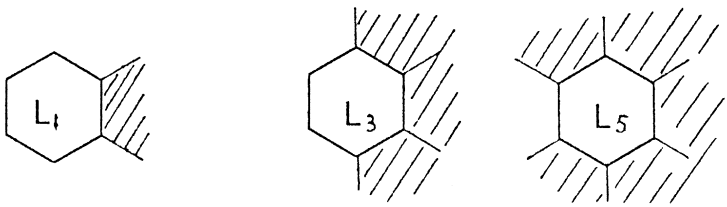

Fig 4

of H. And an edge of H is called a fixed edge, if it is either a fixed single edge or fixed double edge. A hexagonal system is normal if it has no fixed edges; essentially disconnected otherwise. Deleting the fixed single edges and the end vertices of all fixed double edges together with their incident edges from an essentially disconnected hexagonal system H, we get the subgraph of H, each connected component of which is a hexagonal system and is normal (it is thus called a normal component of H). It is well known that an essentially disconnected hexagonal system has at least two normal components. Recently, it is also shown that, if a hexagonal system has a single hexagon as one of its normal components, then it has at least three normal components [3,16].

For normal hexagonal systems, the following fact was always conjectured by Cyvin and Gutman [2] and proved by He and He [5].

Theorem 6. *An arbitrary normal hexagonal system with h hexagons* ($h \geqslant 2$) *must have a hexagon the removal of which from H yields another normal hexagonal system with* $h-1$ *hexagons.*

The above theorem can be used for a simple construction of normal hexagonal systems. A stronger result has been formulated by Hansen and Zheng [3,16]. Therefore, any normal hexagonal system H with $h>1$ hexagons can be written in the form: $H=H_{h-1}+s_h$, where H_{h-1} is a normal hexagonal system of $h-1$ hexagons and s_h is a hexagon of H. The addition of s_h to H_{h-1} has the three possible ways L_1, L_3 and L_5 (see Fig. 4). Repeating the above process, a normal hexagonal system H can be decomposed into the form: $H=s_1+s_2+\cdots+s_h$ such that the s_i's are all hexagons of H and $H_i=s_1+\cdots+s_i$ ($H=H_h, 1\leqslant i\leqslant h$) are all normal hexagonal systems.

Lemma 7. *Let H be a normal hexagonal system with h* (>1) *hexagons. With the above notations, we have that* $C(H_j)\geqslant C(H_i)$ *for* $h\geqslant j\geqslant i\geqslant 1$; *in particular,* $C(H)\geqslant C(H_i)$ *for* $1\leqslant i\leqslant h$.

Proof. It follows immediately from the fact that a Clar formula of H_i is a resonant pattern of H_j. □

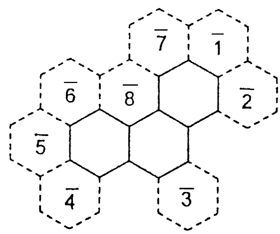

Fig 5

Proof of Theorem 5. By Lemma 1 and Corollary 3, we have:

$$\sigma(H,0) = 1 + a(H,1) + a(H,2) + \cdots + a(H,C(H)),$$
$$\sigma(H,1) = a(H,1) + 2a(H,2) + \cdots + C(H)a(H,C(H)).$$

Since $C(H) \geqslant 2$, then $a(H,2) \geqslant 1$ and

$$\sigma(H,1) - \sigma(H,0) = (a(H,2) - 1) + 2a(H,3) + \cdots + (C(H) - 1)a(H,C(H)) \geqslant 0$$

which implies that $\sigma(H,1) \geqslant \sigma(H,0)$ and if the equality holds then $C(H) = 2$ and $a(H,2) = \sigma(H,2) = 1$. The latter implies that H has a unique Clar formula with 2 hexagons. It can be proved that H is normal. If not, $C(H) = 2$ implies that H has exactly two normal components. If each normal component of H contains more than one hexagon, then H has at least two Clar formulas since each hexagon of a normal hexagonal system is resonant [9], a contradiction; otherwise, H has at least three normal components [3,16], a contradiction. Thus H is normal. Furthermore, a normal hexagonal system H can be decomposed into the form: $H = s_1 + s_2 + \cdots + s_h$ such that the s_i's are hexagons and $H_{i+1} = H_i + s_{i+1}$ are normal hexagonal systems for $i = 1, 2, \ldots, h-1$. For $C(H) \geqslant 1$, there exists a subscript j $(3 \leqslant j \leqslant h)$ such that $H_j = Hl(r_1, r_2)$ (i.e. a hexagonal chain with one kink). Since a Clar formula of H_j is also a Clar formula of H, $a(H,2) = 1$ implies that $H_j = Hl(2,2)$, i.e. $j = 3$. If $h > 3$, s_4 must lie on one of positions $\bar{1}$–$\bar{8}$, which are illustrated in Fig. 5. But the previous seven additions of s_4 to H_3 contradict $C(H) = 2$ or $a(H,2) = 1$. Hence, $H_4 = L_{2,2}$. By an analogous manner, it can be proved that $H = H_4 = L_{2,2}$. On the other hand, $P(Hl(2,2), w) = 5 + 5w + w^2$ and $P(L_{2,2}, w) = 6 + 6w + w^2$. The proof is complete. □

Much evidence support the following unimodal conjecture.

Conjecture 8. The coefficients of Clar covering polynomial of a hexagonal system H are of unimodal, i.e., there exsists a subscript j such that $\sigma(H,C) \leqslant \sigma(H,C-1) \leqslant \cdots \leqslant \sigma(H,j) \geqslant \sigma(H,j+1) \geqslant \cdots \geqslant \sigma(H,0)$, where $C = C(H)$.

Theorem 9. *For any hexagonal systems H with $1 \leqslant C(H) \leqslant 5$, Conjecture 8 is true.*

Proof. Since $1 \leqslant C(H) \leqslant 5$, it is clear that $\lceil (C(H)-1)/2 \rceil = 0$, 1 or 2. By Theorems 4 and 5 the theorem is easily shown to be true. □

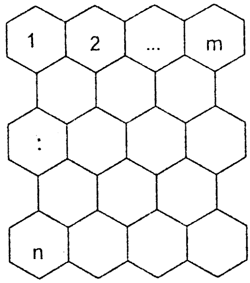

Fig 6 $R^i(m,n)$.

The Clar number of hexagonal systems is an important topological index. Various upper bounds [4,10,13] of the Clar number has been obtained and can be used for constructing Clar formulas of some special types of hexagonal systems. For example, denote by (x,y,z) $(x\leqslant y\leqslant z)$ the invariant triple of H, where x,y and z denote the number of edges of a perfect matching in three edge directions, respectively. Then $C(H)\leqslant x$ [10]. A non-trivial lower bound of the Clar number has not been reported yet. As a by-product of Theorem 2, we have:

Theorem 10. *Let H be hexagonal systems with perfect matching. Then*

$$C(H)\geqslant\left\lceil\frac{h_1(H)}{K(H)-1}\right\rceil,$$

and the equality can be holded.

Proof. By Corollary 3, we have that

$$\sigma(H,1)=h_1(H)=\sum_{k=1}^{C(H)}ka(H,k)\leqslant C(H)\sum_{k=1}^{C(H)}a(H,k)=C(H)(K(H)-1)$$

which yields the lower bound of $C(H)$. In the following we will show that this bound is sharp by an example. Consider a prolate rectangle $R^i(m,n)$ (see Fig. 6), where m and n are positive integers satisfying that $n\leqslant m+1$. It is easy to see that $P(R^i(m,n),w)=(mw+m+1)^n$. Obviously $C(H)\leqslant x=n$. On the other hand,

$$\frac{h_1(H)}{K(H)-1}=\frac{nm(m+1)^{n-1}}{(m+1)^n-1}>n\frac{m}{m+1}=n-\frac{n}{m+1}\geqslant n-1.$$

Therefore,

$$n\geqslant C(H)\geqslant\frac{h_1(H)}{K(H)-1}>n-1,\ \text{i.e. } C(H)=\left\lceil\frac{h_1(H)}{K(H)-1}\right\rceil=n. \qquad \square$$

Finally, we will establish a relation between the Clar covering polynomial and sextet polynomial of a hexagonal system.

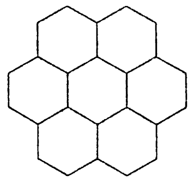

Fig 7 A coronene C.

Theorem 11. *Let H be a hexagonal system with a perfect matching. For all $0 \leqslant i \leqslant C(H)$, $a(H,i) \geqslant s(H,i)$ and all the equalities hold if and only if H has no coronene C (see* Fig. 7*) as its nice subgraph (a subgraph C of H is called a nice subgraph if either $H - C$ has a perfect matching or $H - C$ is empty).*

Proof. For $0 \leqslant i \leqslant C(H)$, denote M_i by a perfect matching containing exactly i proper sextets and S_i the set of all proper sextets of M_i ($S_i = \emptyset$ is allowed). Define a Clar transformation from perfect matcings to resonant patterns as $f_i : M_i \mapsto S_i$. Similar to the proof of Lemma 1, we have that f_i is a surjection, which implies that $a(H,i) \geqslant s(H,i)$ for all $0 \leqslant i \leqslant C(H)$. Thus,

$$K(H) = \sum_{i=0}^{C(H)} a(H,i) \geqslant \sum_{i=0}^{C(H)} s(H,i).$$

There exists a one-to-one correspondence between the perfect matchings and resonant patterns if and only if H has no coronene C as its nice subgraph [8]. Furthermore, for all $0 \leqslant i \leqslant C(H)$ we have that $a(H,i) = s(H,i)$ if and only if H has no coronene as its nice subgraph. □

As an immediate consequence, we have:

Corollary 12. *Let H be a hexagonal system with a perfect matching. Then $\sum_{i=0}^{C(H)} a(H,i)x^i$ is the sextet polynomial of H if and only if H has no coronene as its nice subgraph.*

The Clar covering polynomial has also some correlation to other kinds of graph polynomials, such as matching polynomial, chromatic polynomial, etc. The interested reader may refer to [14]. Much work have been devoted to one-to-one correspondence between (generalized) resonant patterns and perfect matchings of hexagonal systems. The corrected sextet polynomial was introduced. The polynomail $\sum_{i=0}^{C(H)} a(H,i)x^i$ produced here is actually the so-called corrected sextet polynomial. Moreover, $P(H,1)$ can be used for counting the perfect matchings of a certain kind of polyominoes produced within crystal physics [7]. The details will be stated elsewhere.

References

[1] Zhibo Chen, Directed tree structure of the set of Kekulé patterns of polyhex graphs, Chem. Phys. Lett. 115 (3) (1985) 291–293.

[2] S.J. Cyvin, I. Gutman, Number of Kekulé structures as a function of the number of hexagons in benzenoid hydrocarbons, Z. Natursforsh 41 (a) (1986) 1079–1986.

[3] P. Hansen, Maolin Zheng, Normal components of benzenoid systems, Theor. Chim. Acta 85 (1993) 335–344.

[4] P. Hansen, Maolin Zheng, Upper bounds for the Clar number of benzenoid hydrocarbons, J. Chem. Soc. Faraday Trans. 88 (1992) 1621–1625.

[5] W.C. He, W.J. He, Some properties and generation of normal benzenoids, Match 25 (1990) 237.

[6] H. Hosoya, T. Yamaguchi, Sextet polynomial. A new enumeration and proof technique for the resonance theory applied to the aromatic hydrocarbons, Tetrahedron Lett. 52 (1975) 4659–4662.

[7] H. Sachs, H. Zernits, Remark on the dimer problem, Discrete Appl. Math. 51 (1994) 171–179.

[8] Fuji Zhang, Rongsi Chen, A theorem concerning polyhex graphs, Match 19 (1986) 179.

[9] Fuji Zhang, Rongsi Chen, When each hexagon of a hexagonal system covers it, Discrete Appl. Math. 30 (1991) 63–75.

[10] Fuji Zhang, Rongsi Chen, Xiaofeng Guo, I. Gutman, An invariant of Kekulé structures of benzenoid hydrocarbons, J. Serb. Chem. Soc. 51 (1986) 537–543.

[11] Fuji Zhang, Xiaofeng Guo, Directed tree structure of the set of Kekulé patterns of generalized polyhexes graphs, Discrete Appl. Math. 32 (1991) 295–302.

[12] Heping Zhang, The Clar covering polynomial of S, T-isomers, Commun. Math. Chem.(Match) 29 (1993) 189–197.

[13] Heping Zhang, The Clar formula of regular t-tier strip benzenoid systems, Systems Sci. Math. Sci. 8 (4) (1995) 327–337.

[14] Heping Zhang, The Clar covering polynomial of hexagonal system with an application to chromatic polynomial, Discrete Math. 172 (1997) 163–173.

[15] Heping Zhang, Fuji Zhang, The Clar covering polynomial of hexagonal systems I, Discrete Appl. Math. 69 (1996) 147–167.

[16] Maolin Zheng, Perfect Macthings of Benzenoid Systems, Ph. D. Thesis, Rutgers University, 1992.